DOAS measurement of glyoxal as an indicator for fast VOC chemistry in urban air

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We present the first direct measurements of glyoxal (CHOCHO) in the atmosphere, and demonstrate that glyoxal measurements are possible by differential optical absorption spectroscopy (DOAS). Glyoxal was routinely detected during the daytime in Mexico City, where mixing ratios ranged from <0.15ppbv (detection limit) to 1.82ppbv. These time-resolved measurements resolve the rapid diurnal variation of glyoxal, and indicate the onset of volatile organic compound (VOC) oxidation about 1hr after sunrise. The atmospheric lifetime of glyoxal is determined to be 1.3hr for overhead sun conditions. Then elevated glyoxal levels indicate a persistently active VOC chemistry during most of the day.

Glyoxal forms from the oxidation of numerous VOCs, which foster the formation of 'photochemical smog' including ozone and aerosol particles; atmospheric levels are essentially unaffected of direct vehicle emissions in Mexico City. Satellite measurements of glyoxal seem feasible, making possible the better identification of photochemical hot-spots in the Earth's atmosphere.

Open-path emission factors derived from open-path DOAS and FTIR Measurements in Mexico City Metropolitan Area

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Mobile sources are responsible for about 40-80% of VOC (volatile organic compounds), and about 70-80% of NO_x (sum of NO and NO_2) emissions in the Mexico City Metropolitan Area (MCMA) [Molina and Molina 2002]. A major challenge arises from the high variability among emission factors [Zielinska et al. 1996, Sagabriel et al. 1996, Kean et al. 2001] derived from probing of individual vehicles, and the skewness of the distribution of emissions from in-use vehicles [Wenzel et al. 2000]. Emissions of VOCs and NO_x are important – though uncertain – input parameters to modeling photochemical smog formation.

A cost-effective novel approach to derive a fuel based emission inventory of NO_x, SO_2 and numerous VOCs from mobile sources is developed and validated in this paper. It exploits collocated open-path Differential Optical Absorption Spectroscopy (DOAS measured numerous aromatic VOCs, HONO, NO_2, SO_2 and HCHO) and Fourier Transform Infrared (FTIR measured CO, CO_2, NO, HCHO, ethylene, ethene, and total alkanes) spectroscopic measurements. The spatial variability of the vehicle fleet assessed by comparing open-path emission factors measured at two sites within the MCMA.